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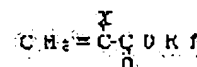
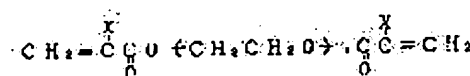
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KAETSU ISAO

(54) OXYGEN PERMEABLE HARD CONTACT LENS

(57)Abstract:

PURPOSE: To provide a hard contact lens made of a polymethyl methacrylate- based material passing a larger amt. of oxygen than polymethyl methacrylate while maintaining the useful characteristics of the polymethyl methacrylate.

CONSTITUTION: When 35-75 pts.wt. methyl methacrylate is radical-copolymerized with 5-40 pts.wt. acrylic (methacrylic) ester represented by formula I and fluoroalkyl acrylate (methacrylate) represented by formula II, they are mixed with 20-120 pts.wt. mixture of an org. solvent incompatible with methyl methacrylate with an org. solvent compatible with methyl methacrylate and the resulting mixture is radical-polymerized to obtain a polymethyl methacrylate copolymer. This copolymer is ground and polished to obtain the objective microporous hard contact lens passing a large amt. of oxygen. In the formula I, X is H or CH₃ and (n) is an integer of 1-10. In the formula II, R_f is a 1-8C fluoroalkyl and X is H or CH₃.



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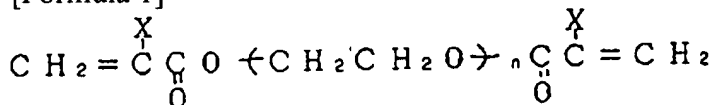
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CLAIMS

[Claim(s)]

[Claim 1] The acrylic (methacrylic) ester 5 thru/ or 40 weight sections expressed with methyl methacrylate 35 thru/ or 75 weight sections, and the following-ization 1 (structure expression 1), The phloroalkyl acrylic (methacrylic) ester 25 thru/ or 50 weight sections expressed with the following-ization 2 (structure expression 2), In carrying out radical copolymerization, 20-120 weight section mixing of the partially aromatic solvent of methyl methacrylate, an immiscible organic solvent, and an organic solvent with compatibility is carried out. It is a hard lens with the large amount of oxygen transparency at the fine porosity obtained grinding and by grinding in the polymethylmethacrylate copolymer obtained by carrying out the radical polymerization of this.

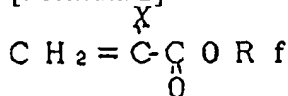
[Formula 1]



構造式 1

ここで X は、 H または、 CH_3 基を
 n は、1 から 10 までの整数を示す。

[Formula 2]



構造式 2

ここでR fは、炭素数1～8のフロロアルキル基を示す。
Xは、H または、CH₃ 基をしめす。

[Claim 2] A hard lens given in the above-mentioned claim to which the above-mentioned methyl methacrylate and an immiscible organic solvent are characterized by carbon numbers being ten or more saturated aliphatic hydrocarbon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a hard lens. Furthermore, when it states in detail, a polymethylmethacrylate copolymer with the large amount of oxygen transparency is related with grinding and the hard lens obtained by grinding with fine porosity.

[0002]

[Description of the Prior Art] It is known well that polymethylmethacrylate occupies the main locations of a hard lens. It is very transparent, and is safe, the grinding for considering as a contact lens and polish are easy, and it is one of the useful hard lenses. However, it also has the fault with it as a hard lens also in polymethylmethacrylate. It is mentioned to one that the own amount of oxygen transparency of polymethylmethacrylate is small. Although it is in the physical properties for which a hard lens is asked variously, the oxygen permeability of a material is observed recently. In order to have worn the contact lens and to protect a cornea from an oxygen deficiency, it is comparatively desirable to have the amount of oxygen transparency with the suitable contact lens material itself for a long period of time.

[0003] From such a purpose, recently, various examination is made in quest of the ingredient with the big amount of oxygen transparency, and an ingredient with the big amount of oxygen transparency is beginning to be developed especially centering on acrylic silicon. However, although the amount of oxygen transparency of the ingredient centering on these acrylic silicon is large compared with polymethylmethacrylate, it is pointed out that it is inferior to polymethylmethacrylate in respect of versatility. There is no reinforcement, crush simply while in use or it is cracked, or when severe, becoming muddy during use etc. is pointed [**** / that the many lack transparency] out. With the ingredient which uses polymethylmethacrylate as a major component from such semantics, the amount of oxygen transparency is large, and if a very transparent and safe ingredient cannot yet appear, but can improve current polymethylmethacrylate and can improve the amount of oxygen transparency, it must be called a wonderful thing.

[0004] The proposal which is going to raise the amount of oxygen transparency is also made by mixing and carrying out the polymerization of the solvent with good compatibility to the monomer which serves as a contact lens ingredient in JP,1-225913,A from such [recently] a viewpoint. However, by this approach, although the amount of oxygen transparency improves a little by mixing a solvent with good compatibility, change of the big amount of oxygen transparency is not expectable into ingredients with the amount of oxygen transparency small from the first, such as PORUME chill methacrylate.

[0005]

[Problem(s) to be Solved by the Invention] As mentioned above, it is the ingredient which uses polymethylmethacrylate as a major component, the amount of oxygen transparency is large, although the very transparent and safe ingredient has not yet appeared, it is extremely meaningful that the amount of oxygen transparency becomes large, and it is an important thing. That is, it is the ingredient which uses polymethylmethacrylate as a major component, and finding out the ingredient with which the useful description of polymethylmethacrylate is owned as it is, and the amount of oxygen transparency exceeds current polymethylmethacrylate is called for.

[0006]

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TECHNICAL FIELD

[Industrial Application] This invention relates to a hard lens. Furthermore, when it states in detail, a polymethylmethacrylate copolymer with the large amount of oxygen transparency is related with grinding and the hard lens obtained by grinding with fine porosity.

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PRIOR ART

[Description of the Prior Art] It is known well that polymethylmethacrylate occupies the main locations of a hard lens. It is very transparent, and is safe, the grinding for considering as a contact lens and polish are easy, and it is one of the useful hard lenses. However, it also has the fault with it as a hard lens also in polymethylmethacrylate. It is mentioned to one that the own amount of oxygen transparency of polymethylmethacrylate is small. Although it is in the physical properties for which a hard lens is asked variously, the oxygen permeability of a material is observed recently. In order to have worn the contact lens and to protect a cornea from an oxygen deficiency, it is comparatively desirable to have the amount of oxygen transparency with the suitable contact lens material itself for a long period of time.

[0003] From such a purpose, recently, various examination is made in quest of the ingredient with the big amount of oxygen transparency, and an ingredient with the big amount of oxygen transparency is beginning to be developed especially centering on acrylic silicon. However, although the amount of oxygen transparency of the ingredient centering on these acrylic silicon is large compared with polymethylmethacrylate, it is pointed out that it is inferior to polymethylmethacrylate in respect of versatility. There is no reinforcement, crush simply while in use or it is cracked, or when severe, becoming muddy during use etc. is pointed [**** / that the many lack transparency] out. With the ingredient which uses polymethylmethacrylate as a major component from such semantics, the amount of oxygen transparency is large, and if a very transparent and safe ingredient cannot yet appear, but can improve current polymethylmethacrylate and can improve the amount of oxygen transparency, it must be called a wonderful thing.

[0004] The proposal which is going to raise the amount of oxygen transparency is also made by mixing and carrying out the polymerization of the solvent with good compatibility to the monomer which serves as a contact lens ingredient in JP,1-225913,A from such [recently] a viewpoint. However, by this approach, although the amount of oxygen transparency improves a little by mixing a solvent with good compatibility, change of the big amount of oxygen transparency is not expectable into ingredients with the amount of oxygen transparency small from the first, such as PORUME chill methacrylate.

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EFFECT OF THE INVENTION

[Effect of the Invention] Thus, the manufacture approach of this invention is the ingredient which uses polymethylmethacrylate as a major component, and made it possible to obtain the hard lens with which the useful description of polymethylmethacrylate is owned as it is, and the amount of oxygen transparency exceeds current polymethylmethacrylate.

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MEANS

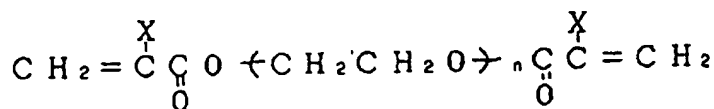
[Means for Solving the Problem] In carrying out radical copolymerization of the phloroalkyl acrylic (methacrylic) ester expressed with the acrylic (methacrylic) ester and the following structure expression 2 which are expressed with methyl methacrylate and the following structure expression 1 mentioned later in this invention, it made it possible to obtain a methyl methacrylate system hard lens with the large amount of oxygen transparency by making into fine porosity the polymethylmethacrylate copolymer obtained by carrying out a radical polymerization, mixing the partially aromatic solvent of methyl methacrylate, an immiscible organic solvent, and an organic solvent with compatibility, and containing this.

[0007] Hereafter, this invention is explained in full detail. The main ingredients which constitute a contact lens from this invention are methyl methacrylate. Polymethylmethacrylate is the ingredient which was excellent in very optical transparency, is safe, and was excellent in the workability as contact RENTZUTO especially grinding, and polish nature, and excelled also in prolonged dimensional stability and a mechanical strength. In this invention, methyl methacrylate is used as a principal component of the contact lens ingredient of this invention from this semantics. In case bulk polymerization of methyl methacrylate is further performed to this useful polymethylmethacrylate by this invention as an approach of raising the amount of oxygen transparency, the partially aromatic solvent of the methyl methacrylate which does not participate in a polymerization, an immiscible organic solvent, and an organic solvent with compatibility tends to be mixed, a radical polymerization tends to be carried out, with this contained, and it is going to obtain a polymethylmethacrylate copolymer with the large amount of oxygen transparency with fine porosity by removing this organic solvent after a polymerization.

[0008] The reason using the partially aromatic solvent of methyl methacrylate, an immiscible organic solvent, and an organic solvent with compatibility is because a polymethylmethacrylate copolymer with the large amount of oxygen transparency is obtained compared with the case where only an organic solvent with good compatibility is mixed as an organic solvent in this invention here. Compared with the case where an organic solvent with good compatibility is probably used, it thinks because big pore has arisen. However, by once containing the organic solvent which does not participate in a polymerization, when two kinds of organic solvents which do not participate in methyl methacrylate and a polymerization were mixed, a radical polymerization is carried out, with this contained and this organic solvent is removed after a polymerization, when the polymethylmethacrylate used as porosity also removes this organic solvent, porosity will become small and will almost return to the original polymethylmethacrylate. For this reason, by this invention, it made it possible to prevent porosity becoming small by removing this organic solvent by carrying out copolymerization of the acrylic (methacrylic) ester shown by the following-ization 3 (structure expression 1) to methyl methacrylate, and making it construct a bridge. However, compared with the case where only an organic solvent with good compatibility is used for the approach using the partially aromatic solvent of the methyl methacrylate of this invention, an immiscible organic solvent, and an organic solvent with compatibility also in this case, it is the description of this invention that the return after removing an organic solvent is also small. The acrylic (methacrylic) ester shown with the following structure expression 1 used by this invention has the functional group of radical polymerization nature equivalent to methyl methacrylate, it is extremely rich in copolymerization nature, and a copolymer gives a transparent ingredient without polymethylmethacrylate and inferiority.

[0009]

[Formula 3]



構造式 1

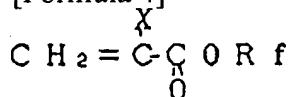
ここで X は、H または、C H₃ 基を
n は、1 から 10 までの整数を示す。

[0010] Moreover, it is two functionality, and excels also in the bridge formation effectiveness, and the acrylic (methacrylic) ester shown with this structure expression 1 is C two H4. Since it has a radical, it excels in a hydrophilic property comparatively, and as a contact lens, compared with polymethylmethacrylate, biocompatibility is considered to be good and may serve as an ingredient which was excellent in a feeling of wearing. C two H4 of the acrylic (methacrylic) ester shown with the above-mentioned structure expression 1 in this invention The value of several n of a radical is limited. That is, the copolymer with the methyl methacrylate which will be obtained if there is more n than 10 is for thermal resistance's falling and making processing of grinding polish etc. difficult. For this reason, by this invention, the number of n is used as range where the range from 1 to 10 is desirable.

[0011] Next, in this invention, further, in order to raise the amount of oxygen transparency, the phloroalkyl acrylic (methacrylic) ester expressed with the following-ization 4 (structure expression 2) is also used as methyl methacrylate and a copolymerization component with the acrylic (methacrylic) ester as which it is indicated with the above-mentioned structure expression 1.

[0012]

[Formula 4]



構造式 2

ここで R f は、炭素数 1 ~ 8 のフロロ
アルキル基を示す。
X は、H または、C H₃ 基をしめす。

[0013] As for the phloroalkyl acrylic (methacrylic) ester expressed with the above-mentioned structure expression 2, it can be equivalent to methyl methacrylate, and it can be extremely rich in copolymerization nature, and a copolymer can give a transparent ingredient without polymethylmethacrylate and inferiority, and the functional group of radical polymerization nature can raise the amount of oxygen transparency further. In the phloroalkyl acrylic (methacrylic) ester expressed with this structure expression 2, as for the phloroalkyl radical Rf, the fluorine permutation alkyl group of carbon numbers 1-8 is used in this invention. When the fluorine permutation alkyl group exceeding 8 is used, although based also on also whenever [fluorine permutation], compatibility with methyl methacrylate may worsen, namely, transparency may be missing. Moreover, grinding and also when polish processing cannot be carried out, it is for being certain at the contact lens which thermal resistance also falls and has precision.

[0014] The phloroalkyl acrylic (methacrylic) ester 25 thru/or 50 weight sections ** to which the ratio of the acrylic (methacrylic) ester shown with methyl methacrylate and the above-mentioned structure expression 1 and the phloroalkyl acrylic (methacrylic) ester expressed with the above-mentioned structure expression 2 is expressed with the acrylic (methacrylic) ester 5 thru/or 40 weight sections expressed with methyl methacrylate 35 thru/or 75 weight sections, and a structure expression 1 by this invention, and a structure expression 2 is used as good range. If the acrylic (methacrylic) ester expressed with the structure expression 1 as a cross linking agent does not fulfill 5 weight sections, in case there will be no bridge formation effectiveness and an organic solvent will be removed, it is because porosity may fully be unable to be held. Moreover, if used exceeding 40 weight sections, while bridge formation will progress too much and resin will become weak conversely, sufficient micropore cannot be opened but it becomes impossible to obtain a polymethylmethacrylate copolymer with the large amount of oxygen transparency. Moreover, the phloroalkyl acrylic (methacrylic) ester expressed with a structure expression 2 If a polymethylmethacrylate copolymer with the desirable large amount of oxygen transparency cannot be obtained unless it fulfills 25 weight sections, but used exceeding 50 weight sections, while thermal resistance will fall An ingredient with good transparency may be hard to be obtained. For this reason, in this invention The phloroalkyl acrylic (methacrylic) ester 25 thru/or 50 weight sections ** expressed with the acrylic (methacrylic) ester 5 thru/or 40 weight sections expressed with methyl methacrylate 35 thru/or 75 weight sections, and a structure expression 1, and a structure expression 2 is used as good range.

[0015] As mentioned above, the partially aromatic solvent of the methyl methacrylate which does not participate in the acrylic (methacrylic) ester shown with methyl methacrylate and a structure expression 1, the phloroalkyl acrylic (methacrylic) ester expressed with a structure expression 2, and a polymerization in this invention, an immiscible organic solvent, and an organic solvent with compatibility is mixed, a radical polymerization is carried out, with this contained, and after a polymerization, this organic solvent tends to be removed and it is going to raise the amount of oxygen transparency of a methyl methacrylate copolymer. Generally the methyl methacrylate which does not participate in the polymerization said by this invention here, an immiscible organic solvent, and the organic solvent with good compatibility can say what has the following property. The polymethylmethacrylate copolymer after 3. radical polymerization which does not check 2. radical polymerization with which the polymethylmethacrylate copolymer after 3. radical polymerization which does not check 2. radical polymerization which mixes the organic solvent with good compatibility to 1. methyl methacrylate and homogeneity mixes a transparent organic solvent immiscible again to methyl methacrylate and homogeneity in 1. monomer phase says an opaque thing.

[0016] It is necessary to use the mixture of two kinds of organic solvents which are satisfied with this invention of this condition of 1-3. That is, when only an organic solvent with good compatibility is used, there is little improvement in the amount of oxygen transparency. On the contrary, when only an immiscible organic solvent is used, the polymethylmethacrylate copolymer after a radical polymerization becomes opaque. In order to enlarge the amount of oxygen transparency by this invention in the range in which the polymethylmethacrylate copolymer after a radical polymerization does not become opaque for this reason, the moderate mixture of methyl methacrylate, an immiscible organic solvent, and an organic solvent with good compatibility is used. Although the ratio of an organic solvent with the good compatibility in this invention and an immiscible organic solvent changes with classes, respectively, generally as for the ratio of an organic solvent with good compatibility, and an immiscible organic solvent, the range of 50 to 50-90 to 10 (weight ratio) is used preferably. If an immiscible organic solvent becomes less than 50 % of the weight, the polymethylmethacrylate copolymer after a radical polymerization will tend to become opaque. Conversely, when there are few immiscible organic solvents than 10%, it is for improvement in the amount of oxygen transparency to decrease. It can be chosen as an organic solvent with the good compatibility said by this invention from the large various ester of the range, alcohol, a ketone, etc., for example. Although it is possible to mention ketones, such as alcohols, such as acetic ester, such as ethyl acetate and butyl acetate, a diethylene glycol, and a butanol, a methyl ethyl ketone, and phenyl methyl ketone, if an example is given, these are examples and this invention is not limited only to these.

[0017] Next, by this invention, aliphatic series higher alcohol, such as long-chain saturated-aliphatic-hydrocarbon compounds, such as Deccan, an undecane, a dodecane, a tridecane, hexadecane, an OKUTA decane, nonadecane, an eicosane, docosane, and tetracosane, decanol, undeca Norian, tridecanol, hexadecanol, stearyl alcohol, eicosa Norian, docosa Norian, and tetracos Norian, etc. can be mentioned to the immiscible organic solvent used by this invention as an example. Especially as for ten or more saturated-aliphatic-hydrocarbon compounds, a carbon number is preferably used abundantly by this invention. Although these also have a solid object in ordinary temperature, when it mixes with an organic solvent with good compatibility, if it is liquefied and is, there will be especially no problem. However, these are examples and this invention is not limited only to these.

[0018] Next, the 20 - 120 weight section is used in per total quantity 100 weight section of the acrylic (methacrylic) ester the amount of these organic solvents used by this invention is indicated to be with methyl methacrylate and a structure expression 1, an organic solvent with good compatibility, and the organic solvent of the sum total of an immiscible organic solvent. Although it will be based also on the class of organic solvent if 20 weight sections are not fulfilled, the amount of oxygen transparency of the methyl methacrylate copolymer made into the purpose of this invention cannot fully be raised. Moreover, if the 120 weight sections are exceeded, a copolymer may be unable to become weak, and it may be unable to be used or processing of grinding, polish, etc. may become difficult. For this reason, by this invention, the total amount of an organic solvent is used per total quantity 100 weight section of the acrylic (methacrylic) ester shown with methyl methacrylate and a structure expression 1, and considering an organic solvent as range where the 20 - 120 weight section is desirable.

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EXAMPLE

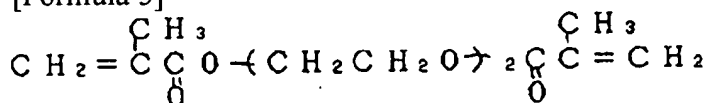
[Example]

Example (1)

The methyl methacrylate 50 weight section, the diethylene-glycol dimethacrylate 20 weight section shown by the following-ization 5 (structure expression 3), 2, 2, 3 and 3, the - tetraphloropropyl methacrylate 30 weight section, the ethyl-acetate 30 weight section, and the dodecane 15 weight section were mixed, and it considered as the uniform monomer solution.

[0021]

[Formula 5]



構造式 3

[0022] In the test tube which added the azobisisobutyronitril of the 1.2 weight section as a polymerization initiator, and carried out the nitrogen purge to this monomer solution, it performed at 60 degrees C for 15 hours, the polymerization was performed at 80 degrees C for 10 hours, and the transparent and colorless cylindrical moldings was obtained. This cylindrical moldings was sliced in thickness of 1mm, and was made immersed at a room temperature into a lot of methanols for 16 hours. Then, the sliced moldings was put in into the vacuum dryer and it was made to dry at 50 degrees C for 5 hours. The physical properties of the sliced moldings which performed this processing are shown below.

Visible-ray permeability 90% oxygen permeability The value of 29x10-11 cc, cm/cm2, sec, and mmHg was shown. In addition, measurement of oxygen permeability was measured using the ***** type oxygen penetrometer. Moreover, grinding and grinding of this sliced moldings were easily completed on the contact lens by the completely same approach as polymethylmethacrylate.

[0023] The example of a comparison (1)

Using the ethyl-acetate 45 weight section, all the back was the same presentations as an example (1), performed the polymerization by the same manufacture approach, and obtained the transparent and colorless cylindrical moldings without using the dodecane 15 weight section in the example (1). This cylindrical moldings was sliced in thickness of 1mm, and was made immersed at a room temperature into a lot of methanols for 16 hours. Then, the sliced moldings was put in into the vacuum dryer and it was made to dry at 50 degrees C for 5 hours. The physical properties of the sliced moldings which performed this processing are shown below.

Visible-ray permeability 90% oxygen permeability The value of 12x10-11 cc, cm/cm2, sec, and mmHg was shown. It has checked that oxygen permeability of the ingredient of this example (1) was improving greatly compared with the ingredient of the example of a comparison (1).

[0024] The example of a comparison (2)

The methyl methacrylate 52 weight section, pentaethylene glycol diacrylate 13 weight section [which is shown by the following-ization 6 (structure expression 4)], 2, 2, 3, 4 and 4, and 4-hexaphlorobuthyl methacrylate 35 weight section, the methyl-butyl-ketone 35 weight section, and the stearyl alcohol 30 weight section were mixed, and it considered as the uniform monomer solution.

[0025]

[Formula 6]



構造式 4

[0026] In the test tube which added the azobisisobutyronitril of the 1.2 weight section as a polymerization initiator, and carried out the nitrogen purge to this monomer solution, it performed at 60 degrees C for 15 hours, the polymerization was performed at 80 degrees C for 10 hours, and the transparent and colorless cylindrical moldings was obtained. This cylindrical moldings was sliced in thickness of 1mm, and was made immersed at a room temperature into a lot of methanols for 16 hours. Then, the sliced moldings was put in into the vacuum dryer and it was made to dry at 50 degrees C for 5 hours. The physical properties of the sliced moldings which performed this processing are shown below.

visible-ray permeability 89% oxygen permeability 34×10^{-11} cc, cm/cm², sec, and mmHg -- the approach as polymethylmethacrylate that this sliced moldings is completely the same again -- a contact lens -- easy -- grinding -- it was able to grind.

[0027] The example of a comparison (2)

Using the methyl-butyl-ketone 60 weight section, all the back was the same presentations as an example (2), performed the polymerization by the same manufacture approach, and obtained the transparent and colorless cylindrical moldings without using the stearyl alcohol 30 weight section in the example (2). This cylindrical moldings was sliced in thickness of 1mm, and was made immersed at a room temperature into a lot of methanols for 16 hours. Then, the sliced moldings was put in into the vacuum dryer and it was made to dry at 50 degrees C for 5 hours. The physical properties of the sliced moldings which performed this processing are shown below.

Visible-ray permeability 90% oxygen permeability The value of 16×10^{-11} cc, cm/cm², sec, and mmHg was shown. It has checked that oxygen permeability of the ingredient of this example (2) was improving greatly compared with the ingredient of the example of a comparison (2).

[Translation done.]